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(54) Method and apparatus for treating a waste gas containing fluorine-containing compounds

(57) The improved apparatus for treatment of a waste gas containing fluorine-containing compounds comprises solids treating means 1 for separating the solids from a waste gas containing fluorine-containing compounds, addition means for adding H₂ and/or H₂O or H₂ and/or H₂O and O₂ as a decomposition assist gas to the waste gas leaving the solids treating means, ther-

mal decomposing means 3 that is packed with γ -alumina 2 heated at 600 - 900°C and which thermally decomposes the waste gas to which the decomposition assist gas has been added, acidic gas treating means 5 for removing acidic gases from the thermally decomposed waste gas, and channels for connecting these means in sequence. The apparatus preferably includes air ejector 7 capable of adjusting its internal pressure.

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Description

[0001] This invention relates to the treatment of a waste gas containing fluorine-containing compounds. More particularly, it relates to a method and an apparatus for efficient treatment of emissions from semiconductor fabrication plants, particularly from the steps of dry cleaning the inner surface of a fabrication apparatus and etching various kinds of deposited films with perfluorocarbons (PFCs) and halogenated hydrocarbons such as C_2F_6 , C_3F_8 , CHF_3 , SF_6 and NF_3 , said waste gases containing not only PFCs but also oxidizing gases such as F_2 , Cl_2 and Br_2 , acidic gases such as HF , HCl , HBr , SiF_4 , $SiCl_4$, $SiBr_4$ and COF_2 , as well as CO .

[0002] Semiconductor fabrication plants use many kinds of harmful gases that can potentially pollute the environment. PFCs contained in waste gases that typically result from the etching and CVD steps are suspected of causing global warming and it is urgently needed to establish an effective system for their removal.

[0003] Various breaking and recovery techniques have heretofore been proposed for PFC removal. Catalytic thermal decomposition is one of the breaking techniques and uses versatile compounds such as Pt catalyst, zeolite-base catalysts, activated charcoal, activated alumina, alkali metals, alkaline earth metals and metal oxides. However, none of these catalytic compounds have proved completely satisfactory.

[0004] The waste gases discharged from the semiconductor fabrication process contain not only PFCs but also oxidizing gases such as F_2 , Cl_2 and Br_2 , acidic gases such as HF , HCl , HBr , SiF_4 , $SiCl_4$, $SiBr_4$ and COF_2 , as well as CO ; however, no method has yet been established that can realize a thorough and effective treatment of these harmful gases.

[0005] If one wants to treat oxidizing gases such as F_2 , Cl_2 and Br_2 by a wet method, thorough treatment cannot be achieved by the sole use of water. If alkali agents or reducing agents are also used, not only process control but also the treatment apparatus becomes complicated and, in addition, the cost of treatment increases.

[0006] To remove CO , it has to be decomposed with oxidizers such as those based on Cu or Mn . As for PFCs, it has been proposed to use alumina as an agent for removing them (Japanese Patent Public Disclosure No. 286434/1998) and this method is characterized by contacting C_2F_6 with molecular oxygen. However, the lifetime of alumina is very short and the throughput or the amount of C_2F_6 that can be treated for 100% decomposition is only 4.8 L/L; what is more, no effective way has been proposed to deal with CO that occurs as a by-product of C_2F_6 decomposition, still less for the oxidizing gases and acidic gases that occur concomitantly with PFCs.

[0007] The present invention has been accomplished under these circumstances and has as an object providing a method for treating waste gases containing flu-

orine-containing compounds which achieves high percent decomposition of PFCs, which proves effective for a prolonged time and which simultaneously realizes effective removal of oxidizing gases, acidic gases and CO that are contained in the waste gases.

[0008] Another object of the invention is to provide an apparatus for implementing this method.

[0009] The first object of the invention can be attained by a method for treatment of a waste gas containing fluorine-containing compounds which comprises the steps of separating the solids from the waste gas, adding H_2 and/or H_2O or H_2 and/or H_2O and O_2 as a decomposition assist gas, thermally decomposing the waste gas by contact with γ -alumina at usually at 500 - 1000°C, preferably 600 - 900°C, more preferably 700 - 900°C, and removing acidic gases from the decomposed waste gas.

[0010] In this method, the waste gas containing fluorine-containing compounds may be a waste gas from a semiconductor fabrication process that contains not only perfluorocarbons and fluorinated hydrocarbons but also oxidizing gases, acidic gases and CO .

[0011] The second object of the invention can be attained by an apparatus for treatment of a waste gas containing fluorine-containing compounds which comprises a solids treating means for separating the solids from a waste gas containing fluorine-containing compounds, an addition means for adding H_2 and/or H_2O or H_2 and/or H_2O and O_2 as a decomposition assist gas to the waste gas leaving the solids treating means, a thermal decomposing means that is packed with γ -alumina heated at 600 - 900°C and which thermally decomposes the waste gas to which the decomposition assist gas has been added, an acidic gas treating means for removing acidic gases from the thermally decomposed waste gas, and channels for connecting these means in sequence.

[0012] In this treatment apparatus, a water scrubber may be used as the solids treating means or the acidic gas treating means. This treatment apparatus may have not only an air ejector capable of adjusting the pressure in the apparatus through which the waste gas passes but also an FT-IR analyzer for controlling the emission density of the treated gas.

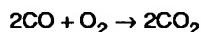
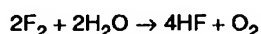
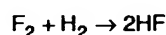
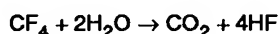
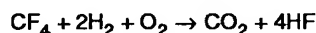
[0013] The first step in the method of the invention for treating a waste gas containing fluorine-containing compounds is passing the waste gas through a solids treating means such as a water scrubber. The exit gas is passed through a thermal decomposing means packed with γ -alumina heated at 500 - 1000°C, preferably 600 - 900°C, and more preferably 700 - 900°C, with H_2 and/or H_2O or H_2 and/or H_2O and O_2 being added as a decomposition assist gas, so that PFCs, oxidizing gases and CO are completely decomposed into acidic gases and CO_2 . The generated acidic gases are removed with an acidic gas treating means such as a water scrubber. The invention may incorporate not only an air ejector capable of adjusting the pressure in the apparatus through which the waste gas passes but also an FT-IR

analyzer for controlling the emission density of the treated gas.

[0014] Fig. 1 is a flowsheet for the waste gas treatment apparatus of the invention.

[0015] The present invention is described below in detail. In the first step, a waste gas containing PFCs, oxidizing gases, acidic gases and CO is passed through a solids treating means such as a water scrubber in order to remove not only the solids such as SiO₂ in the waste gas but also Si compounds such as SiF₄, SiCl₄ and SiBr₄ that may potentially solidify in the thermal decomposing means at the next stage. If the waste gas is directly introduced into the thermal decomposing means without being passed through the solids treating means, clogging or other blocking problems will occur, potentially preventing the waste gas from smoothly flowing through the packed γ-alumina layer. The performance of γ-alumina may also deteriorate. By passing the waste gas through the solids treating means, the solids and the acidic gases containing Si compounds are removed whereas part of oxidizing gases such as F₂, Cl₂ and Br₂ as well as all volumes of PFCs and CO are discharged.

[0016] The waste gas emerging from the solids treating means is then introduced into the thermal decomposing means so that it is decomposed through contact with γ-alumina heated at 500 - 1000°C, preferably 600 - 900°C, more preferably 700 - 900°C. On this occasion, H₂ and/or H₂O; or H₂ and/or H₂O and O₂ are added to the waste gas as a decomposition assist gas so that the components of the waste gas are decomposed into acidic gases and CO₂ according to the following reaction schemes:



[0017] Thus, PFC reacts with H₂ and O₂ or H₂O to be decomposed into CO₂ and HF. Acidic gases such as F₂ react with H₂ or H₂O to be decomposed to another acidic gas HF. Carbon monoxide (CO) is oxidized to CO₂.

[0018] As for PFC, H₂ or H₂O is added in moles at least equal to the moles necessary for the F atoms in the PFC to be converted to HF and O₂ is added in moles at least equal to the moles necessary for the C atoms in the PFC to be converted to CO₂. Preferably, O₂ is added in moles which are at least equal to the sum of

one mole and the above-defined minimum number of moles. As for oxidizing gases, H₂ is introduced in moles at least equal to the moles necessary for the halogen atoms (X) in the oxidizing gas to be converted to an acidic gas (HX).

[0019] The waste gas leaving the thermal decomposing means only contains the acidic gases (HX) and CO₂ and by subsequent treatment with an acidic gas treating means such as a water scrubber, the acidic gases are completely removed.

[0020] The alumina to be used in the invention may have a γ-crystalline structure without a uniform pore distribution. While the shape of the alumina is not limited in any particular way, spheres are easy to handle and, hence, preferred. To the extent that will not unduly increase the resistance to the passage of the waste gas, the particle size of γ-alumina should be as small as possible, preferably between 0.8 mm and 2.6 mm. The γ-alumina may be held at between 500°C and 1000°C, preferably 600°C and 900°C and more preferably 700°C and 900°C during the passage of the waste gas.

[0021] The solids treating means and the acidic gas treating means are preferably a packed column or a spray column on the condition that they are adapted to spray water. The thermal decomposing means should be adapted to permit the introduction of H₂ and/or H₂O or H₂ and/or H₂O and O₂ as a decomposition assist gas.

[0022] Fig. 1 is a flowsheet for the waste gas treatment apparatus of the invention. It generally comprises the solids treating means 1, the γ-alumina packed layer 2, the thermal decomposing means 3, a cleaning water circulating pump 4, the acidic gas treating means 5, an FT-IR analyzer 6, an air ejector 7 and a bypass valve 8.

[0023] A waste gas 9 containing PFCs, oxidizing gases, acidic gases and CO is first passed through the spray column (solids treating means) 1 so as to remove the solids and Si compounds. The waste gas is then passed through the thermal decomposing means 3 which is also supplied with H₂, O₂ and H₂O to decompose the PFCs, oxidizing gases and CO into acidic gases and CO₂. The acidic gases are removed by passage through the next spray column (acidic gas treating means) 5, from which the treated gas 10 emerges.

[0024] The air ejector 7 is installed to control the pressure in each of the treating means and the FT-IR analyzer 6 is provided to monitor the treated gas.

[0025] Spray water 11 is introduced into the acidic gas treating means 5 and the spent water is forced to the solids treating means 1 with the cleaning water circulating pump 4; the water is used in spraying there and discharged as wastewater 12.

[0026] The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

Example 1

[0027] A quartz column of 25 mm ϕ was packed with

γ -alumina to a height of 100 mm. The γ -alumina was a commercial product of Mizusawa Kagaku K.K. (NE-OBEAD GB-08) having a particle size of 0.8 mm. The quartz column was installed in a ceramic electric furnace and the alumina layer was heated at 800°C.

[0028] In addition to CF_4 diluted with N_2 gas, H_2 and O_2 were supplied as decomposition assist gases, the amount of H_2 being such that the number of H atoms was at least equal to the number of F atoms in CF_4 and the amount of O_2 being at least equimolar to the amount of H_2 introduced. These gases were flowed into the column at a total rate of 408 sccm and their entrance concentrations were 1% (CF_4), 3.0% (H_2) and 5.7% (O_2).

[0029] In order to evaluate the performance of the treatment system, the exit gas was analyzed periodically and the passage of the CF_4 gas was stopped when the removal of CF_4 dropped below 98%. The throughput was determined from the amount of CF_4 that had been passed through the system. The analysis of CF_4 and other gases was conducted with a gas chromatographic apparatus equipped with a mass detector.

[0030] As it turned out, the removal of CF_4 dropped to 98% when its passage continued for 920 min. At this point in time, the throughput as determined from the quantity of the supplied CF_4 was 77 L/L. Throughout the experiment, the concentration of CO emission was below the tolerable level (25 ppm).

Comparative Example 1

[0031] An experiment was conducted using the same equipment as in Example 1 that was packed with the same γ -alumina in the same amount and heated to the same temperature. The total gas flow rate was 408 sccm; the feed gas was a mixture of N_2 -diluted CF_4 and SiF_4 ; in addition, H_2 and O_2 were supplied as decomposition assist gases, the amount of H_2 being such that the number of H atoms was at least equal to the total number of F atoms in CF_4 and SiF_4 and the amount of O_2 being at least equimolar to the amount of H_2 introduced. These gases were flowed into the column at respective concentrations of 0.95% (CF_4), 0.97% (SiF_4), 5.3% (H_2) and 6.0% (O_2).

[0032] As it turned out, the removal of CF_4 dropped below 98% when the passage of the CF_4/SiF_4 gas continued for 510 minutes. At this point in time, the throughput was 40 L/L, which was nearly one half the throughput for the case where only CF_4 gas was supplied. Throughout the experiment, the concentration of CO was below the tolerable level.

Example 2

[0033] An experiment was conducted using the same equipment as in Example 1 that was packed with the same γ -alumina in the same amount and heated to the same temperature. The total gas flow rate was 408 sccm; the feed gas was a mixture of N_2 -diluted CF_4 and

F_2 ; in addition, H_2 and O_2 were supplied as decomposition assist gases, the amount of H_2 being such that the number of H atoms was at least equal to the total number of F atoms in CF_4 and F_2 and the amount of O_2 being at least equimolar to the amount of H_2 introduced. These gases were flowed into the column at respective concentrations of 0.92% (CF_4), 1.1% (F_2), 5.0% (H_2) and 6.0% (O_2).

[0034] As it turned out, the removal of CF_4 dropped below 98% when the passage of the CF_4/F_2 gas continued for 25 hours. At this point in time, the throughput was 115 L/L, which was 1.51 times higher than the throughput for the case where only CF_4 gas was supplied. Throughout the experiment, the concentrations of CO and F_2 were below the tolerable levels (1 ppm for F_2), provided that F_2 had been decomposed into HF.

Reference Example 1

[0035] An experiment was conducted using the same equipment as in Example 1 that was packed with the same γ -alumina in the same amount and heated to the same temperature. The total gas flow rate was 408 sccm; in addition to N_2 -diluted CO, O_2 was supplied in moles at least equal to the moles necessary for CO to be converted to CO_2 ; their respective entrance concentrations were 1.4% (CO) and 5.7% (O_2). Throughout the passage of the feed gas for 30 minutes, the concentration of CO was below the detection limit (2 ppm); all of CO had been oxidized to CO_2 .

Comparative Example 2

[0036] An experiment was conducted using the same equipment as in Example 1 that was packed with the same γ -alumina in the same amount and heated to the same temperature. The total gas flow rate was 408 sccm; in addition to N_2 -diluted CO, H_2O was supplied at a rate of 0.090 mL/min which was 22 times as much as CO; the entrance concentration of CO was 1.3%.

[0037] As it turned out, 1000 ppm of CO leaked as a result of 15-min passage of the feed gas. Obviously, the concentration of CO could not be reduced to below the tolerable level (25 ppm) by the sole addition of H_2O .

Reference Example 2

[0038] An experiment was conducted using the same equipment as in Example 1 that was packed with the same γ -alumina in the same amount and heated to the same temperature. The total gas flow rate was 408 sccm; in addition to N_2 -diluted CO, H_2O was supplied at a rate of 0.090 mL/min which was 18 times as much as CO and O_2 was supplied in moles at least equal to the moles necessary for CO to be converted to CO_2 ; the entrance concentrations of CO and O_2 were 1.5% and 3.4%, respectively.

[0039] As it turned out, the concentration of CO had

been reduced to below the detection limit (2 ppm) after the passage of the feed gas for 3 hours. Obviously, CO was oxidized to CO₂ by addition of O₂.

Example 3

[0040] An experiment was conducted using the same equipment as in Example 1 that was packed with the same γ -alumina in the same amount and heated to 700°C. The total gas flow rate was 408 sccm; in addition to N₂-diluted CF₄, H₂O was supplied at a rate of 0.040 mL/min which was 14 times as much as CF₄ and O₂ was supplied in moles at least equal to the moles necessary for the C atom in CF₄ to be converted to CO₂; the entrance concentrations of CF₄ and O₂ were 0.89% and 3.0%, respectively.

[0041] As it turned out, the removal of CF₄ dropped below 98% when the passage of the feed gas continued for 23 hours. At this point in time, the throughput was 110 L/L, which was 1.4 times higher than the throughput of CF₄ treatment in the presence of added H₂ and O₂. Throughout the experiment, the concentration of CO was below the tolerable level.

Comparative Example 3

[0042] In order to evaluate the effectiveness of the wet process in treating oxidizing gases and acidic gases, a water cleaning column (210 mm ϕ x 430 mm^H with a Raschig ring packed to a height of 170 mm) was supplied with a waste gas at a total rate of 60 L/min and spray water at a rate of 3.5 L/min. The waste gas was prepared from F₂, SiF₄ and Cl₂ which had entrance concentrations of 1100 ppm, 1600 ppm and 5100 ppm, respectively. At the exit of the column, F₂, SiF₄ and Cl₂ were detected at concentrations of 11 ppm, < 1 ppm, and 3300 ppm, respectively. Obviously, SiF₄ was effectively treated but F₂ and Cl₂ leaked out.

Example 4

[0043] A water cleaning column (210 mm ϕ x 430 mm^H with a Raschig ring packed to a height of 170 mm) was used as a solids treating means. This column was combined with a thermal decomposing means comprising a preheating chamber and a catalyst packed chamber and an acidic gas treating means which was the same as the water cleaning column. The exit gas leaving the acidic gas treating means was monitored with an FT-IR analyzer (Infinity 6000 of MATTSON) and the pressure in the experimental system was controlled with an air ejector of Daito Seisakusho K.K. The solids treating means and the acidic gas treating means were supplied with cleaning water at respective flow rates of 2 L/min and 4 L/min. The thermal decomposing means was supplied with air and pure water at respective flow rates of 10 L/min and 2.4 mL/min. The catalyst was 15 L of γ -alumina (NEOBEAD GB-08 of Mizusawa Kagaku K.K.)

[0044] A gas dryer (MD-70-72P of PERMAPUR) was installed ahead of the FT-IR analyzer for removing the moisture in the waste gas. Air was supplied into the air ejector at a rate of 30 L/min so that the pressure in the system was kept at a negative value of -0.5 kPa. A waste gas was introduced at a flow rate of 60 L/min and it was prepared from a N₂ base containing CF₄, SiF₄, F₂ and CO at respective concentrations of 0.5%, 0.3%, 0.3% and 0.3%. The waste gas was first passed through the solids treating means, then passed through the thermal decomposing means in the presence of added water and O₂, with the catalyst bed being heated at 700°C. The waste gas was subsequently passed through the acidic gas treating means and the treated gas was continuously analyzed by FT-IR. After the passage of the waste gas for 10 hours, CO₂ was detected in an amount of 6900 ppm but each of CF₄, SiF₄, HF and CO had been treated to below 1 ppm. No F₂ was detected by ion chromatographic analysis.

Example 5

[0045] A waste gas treatment was conducted with the same experimental setup under the same conditions as in Example 4, except that CF₄ was replaced by C₂F₆ and that the waste gas was prepared from a N₂ base containing C₂F₆, SiF₄, F₂ and CO at respective concentrations of 0.5%, 0.3%, 0.3% and 0.3%. The waste gas was passed through the solids treating means, the thermal decomposing means and the acidic gas treating means.

[0046] The treated gas emerging from the acidic gas treating means was continuously analyzed by FT-IR. After the passage of the waste gas for 10 hours, CO₂ was detected in an amount of 11000 ppm but each of C₂F₆, SiF₄, HF and CO had been treated to below 1 ppm. No F₂ was detected by ion chromatographic analysis.

[0047] According to the invention, harmful waste gases from the semiconductor fabrication process that contain PFCs, oxidizing gases, acidic gases and CO and which are a potential accelerator of global warming can be treated in such a way that high percent decomposition is maintained for a prolonged time.

Claims

1. A method for treatment of a waste gas containing fluorine-containing compounds which comprises the steps of separating the solids from the waste gas, adding H₂ and/or H₂O or H₂ and/or H₂O and O₂ as a decomposition assist gas, thermally decomposing the waste gas by contact with γ -alumina at 500 - 1000°C, and removing acidic gases from the decomposed waste gas.
2. The method according to claim 1, wherein the temperature used in the thermally decomposing step

ranges from 600 - 900°C

3. The method according to claim 1, wherein said waste gas containing fluorine-containing compounds contains perfluoro-carbons and fluorinated hydrocarbons as well as oxidizing gases, acidic gases and CO. 5
4. The method according to claim 3, wherein said waste gas containing fluorine-containing compounds is a waste gas from a semiconductor fabrication process. 10
5. An apparatus for treatment of a waste gas containing fluorine-containing compounds which comprises a solids treating means for separating the solids from a waste gas containing fluorine-containing compounds, an addition means for adding H₂ and/or H₂O; or H₂ and/or H₂O and O₂ as a decomposition assist gas to the waste gas leaving the solids treating means, a thermal decomposing means that is packed with γ -alumina heated at 500 - 1000°C and which thermally decomposes the waste gas to which the decomposition assist gas has been added, an acidic gas treating means for removing acidic gases from the thermally decomposed waste gas, and channels for connecting these means in sequence. 15 20 25
6. The apparatus according to claim 5, wherein said solids treating means or said acidic gas treating means is a water scrubber. 30
7. The apparatus according to claim 5 or 6, which has not only an air ejector capable of adjusting the pressure in the apparatus through which the waste gas passes but also an FT-IR analyzer for controlling the emission density of the treated gas. 35

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Fig. 1